

Docket No.: H0610.0352/P352  
(PATENT)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of:  
Kim Aasberg-Petersen, et al.

Application No.: Not Yet Assigned

Filed: Concurrently Herewith

Art Unit: N/A

For: PROCESS FOR THE PRODUCTION OF  
SYNTHESIS GAS

Examiner: Not Yet Assigned

**CLAIM FOR PRIORITY AND SUBMISSION OF DOCUMENTS**

MS Patent Application  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

Applicant hereby claims priority under 35 U.S.C. 119 based on the following  
prior foreign application filed in the following foreign country on the date indicated:

<u>Country</u>	<u>Application No.</u>	<u>Date</u>
Denmark	PA 2002 01435	September 26, 2002

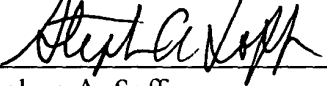
Application No.: Not Yet Assigned

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In support of this claim, a certified copy of the said original foreign application is filed herewith.

Dated: September 23, 2003

Respectfully submitted,

By 

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# Kongeriget Danmark

Patent application No.: PA 2002 01435  
Date of filing: 26 September 2002  
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Title: Fremgangsmåde til fremstilling af syntesegas

IPC: C01B 3/38; B01J 8/04

This is to certify that the attached documents are exact copies of the above mentioned patent application as originally filed.



**Patent- og  
Varemærkestyrelsen**  
Erhvervsministeriet

13 August 2003

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26 September 2002

DK375-7237003

HABS/SSN/AKN

**Process for the Production of Synthesis Gas**

GB-281

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The invention concerns the production of synthesis gas by a sequence of endothermic and/or adiabatic steam reforming and autothermal steam reforming.

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#### Background of the Invention

US Patent No. 6,375,916 discloses a method for preparing synthesis gas by installing a pre-reformer upstream an autothermal reformer (ATR). The pre-reformer is used to re-  
10 move or reduce the contents of higher hydrocarbons from a hydrocarbon feed stream with the advantage that lower steam to carbon ratios can be employed without soot formation in the ATR. However, the process described is not able to produce a synthesis gas with an hydrogen-to carbon monoxide  
15 ratio close to 2.0 unless either the steam-to-carbon ratio is very low (probably less than 0.2) or the difference between the exit temperature from and the inlet temperature to the ATR is very high. In the former case this may give difficulties with operating the prereformer without carbon  
20 formation and in the latter case the amount of oxygen used may be disadvantageously high.

US Patent application 20010051662 by Arcuri et al. discloses a method to produce synthesis gas involving among  
25 others the mixing of tail gas and a hydrocarbon feedstock and feeding the resultant mixture to an adiabatic pre-reformer. The effluent from the adiabatic pre-reformer is passed to a synthesis gas generator for production of synthesis gas.

30

If the synthesis gas generator is an autothermal reformer, a synthesis gas with a hydrogen to carbon monoxide ratio of

about 2.0 can be produced. However, recirculation of the tail gas to the adiabatic pre-reformer is disadvantageous consumption is higher if tail gas is added downstream the adiabatic steam reformer.

5

### Summary of the Invention

The invention is a process for the production of synthesis gas from a hydrocarbon feed stock comprising the steps of  
10 endothermic and/or adiabatic catalytic steam reforming and autothermal steam reforming in series, wherein the steam reforming is carried out in one or more endothermic stages in series and/or in one or more adiabatic steam reforming stages in series with intermediate heating of feed stock  
15 gas leaving the adiabatic reforming stages and wherein carbon monoxide rich gas is added prior to at least one of the endothermic or adiabatic steam reforming stages and/or prior to the autothermal steam reforming step.

20 A plant for production of synthetic diesel and other synthetic hydrocarbons consists of three main units. In the first main unit synthesis gas (a mixture of hydrogen and carbon oxides) is produced from the feedstock which is usually natural gas or a similar light hydrocarbon feedstock.  
25 In the second main unit, the actual hydrocarbon synthesis takes place usually by the Fischer-Tropsch synthesis. In the final unit often known as the Product Work-up unit the raw products are refined and /or separated to give the desired end products. The present invention relates to an improved method for production of synthesis gas.  
30

Today one of the most cost effective and efficient methods for production of synthesis gas is by Autothermal Reforming (ATR). In ATR the light hydrocarbon feedstock with addition of steam reacts with a sub-stoichiometric amount of oxygen to produce synthesis gas. An ATR reactor consists of a burner, a combustion chamber, and a catalyst bed in a refractory lined pressure shell. The ATR reactor is a conventional process unit.

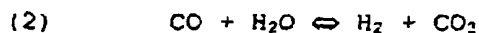
- 10 For the Fischer-Tropsch synthesis to be as effective as possible, a specific synthesis gas composition is often desired. In many cases the desired synthesis gas composition is given by the ratio of the hydrogen content to the carbon monoxide content. The desired ratio is often approximately
- 15 2.0. With most operating conditions ATR is not able to produce this ratio. Instead a carbon dioxide-containing stream must be recirculated to a location upstream the ATR reactor. This recirculation stream is often a tail gas, which is essentially a byproduct from the Fischer-Tropsch synthesis unit and/or the Product Work-up unit. The main components in the tail gas are carbon monoxide, carbon dioxide, hydrogen and various light paraffinic and olefinic hydrocarbons.
- 20
- 25 Synthesis gas production may account for more than 50% of the total capital cost in a Fischer-Tropsch plant. For a plant based on ATR a large fraction of the cost of the synthesis gas production unit arises from the air separation unit needed to produce oxygen. Hence, there is a considerable interest in methods for reducing the oxygen consumption per unit of synthesis gas produced.
- 30

Increasing the temperature of the hydrocarbon feedstock before it enters the ATR reactor and/or reducing the steam-to-carbon (S/C) ratio reduces the oxygen consumption. The S/C-ratio is defined as the ratio of the amount of steam to carbon in the hydrocarbon feedstock. Both of the described methods have disadvantages. Increasing the feedstock temperature increases the risk of cracking of the hydrocarbons in the feedstock and means that more expensive materials must be used in the heaters or heat exchangers upstream the ATR. Reducing the S/C-ratio decreases the margin to soot formation in the ATR and may also increase the risk of cracking of hydrocarbons in heaters or heat exchangers upstream the ATR. The present invention concerns a process whereby both of these disadvantages are avoided while the oxygen consumption is reduced considerably.

According to the present invention a reformer unit is placed before and in series with the ATR reactor. The reformer unit receives heat from a hot process gas stream and steam reforming of hydrocarbons takes place in the reformer unit as illustrated below for methane:



The steam reforming reaction is accompanied by the Shift Reaction:



The above two reactions are in most cases close to equilibrium at the reformer unit outlet. If higher hydrocarbons (hydrocarbons with 2 or more hydrocarbon atoms) are present in the reformer unit feed stream, these are also steam reformed according to reactions similar to the above.



It is described in the art (e.g. US patent No. 6,375,916) that a pre-reformer can be placed upstream the ATR in a Fischer-Tropsch plant. In this case, the reformer unit is placed between the pre-reformer and the ATR, i.e. in series and downstream the pre-reformer and in series and upstream the ATR. Regardless of whether an adiabatic pre-reformer is present, tail gas can be added before and/or after the reformer unit.

Addition of a reformer unit upstream the ATR provides a means for adding heat into the ATR feed stream while maintaining a reasonable temperature at the ATR reactor inlet. At the same time the margins to the soot points for the ATR are increased and the risk of cracking from hydrocarbons in the ATR feed stream is reduced. Furthermore, the oxygen consumption per unit of produced synthesis gas is decreased without substantially affecting the synthesis gas composition.

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#### **Brief Description of the Drawings**

Fig. 1 shows the overall process scheme with the reformer unit.

Fig. 2 shows a specific embodiment of the process.

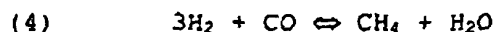
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#### **Detailed Description of the Invention**

A description of the process scheme with the reformer unit is given in Fig. 1. Desulphurised natural gas (1) or a similar feedstock is mixed with steam (2) and preheated in the heat exchanger or heater (3) to the desired inlet temperature to the adiabatic pre-reformer (4). This tempera-

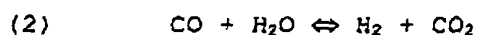
ture is typically between 320-550°C. In the pre-reformer

(4) the following reactions take place:



At most conditions higher hydrocarbons (hydrocarbons with more than 1 carbon atom) are completely removed. The last two reactions (4) and (2) are close to equilibrium at the exit temperature of the adiabatic pre-reformer (4). Typically, the catalyst in the adiabatic pre-reformer is nickel on a ceramic carrier.

Tail gas (5) heated in heater or heat exchanger (12) may optionally be added through line (6) to the pre-reformer effluent (21) to form the reformer unit feed stream (20). In the reformer unit (8) the reformer unit feed stream is steam reformed according to the following reactions:



At most conditions the reformer unit effluent (22) will be virtually free of higher hydrocarbons and reactions (1) and (2) above will be close to thermodynamic equilibrium. Most preferably, the reformer unit effluent (22) will have a temperature between 500°C and 750°C. The heat for the endothermic steam reforming reactions and for the heating is supplied by heat exchange with a hot process gas stream (not shown in Fig. 1).

Heated tail gas is optionally added to the reformer unit effluent through line (7) resulting in an ATR feed stream (23). The ATR feed stream (23) and oxidant (10) usually containing more than 90% oxygen is passed to the autothermal reformer (9) in which synthesis gas is produced and withdrawn as product (11), which is sent to the Fischer-Tropsch synthesis section. The total amount of tail gas added through line (6) and/or (7) is adjusted to give the desired exit gas composition from the autothermal reformer (9).

Steam reforming involves the risk of detrimental carbon formation on the catalyst. For methane, this is expressed by:



The catalyst in the reformer unit may be either nickel-based catalysts and/or catalysts based on noble metals. With noble metals it is possible to operate with lower steam-to-carbon ratios without detrimental carbon formation on the catalyst as described in the art, e.g. Rostrup-Nielsen et al., J. of Catalysis 144, pages 38-49, 1993. Often, the required amount of steam to avoid carbon formation increases with increasing temperature. Hence, in one embodiment of the present invention Nickel can be used at the zones in the reformer unit operating at lower temperature, while noble metals can be used in the zones operating at higher temperatures.

The hydrogen content in the gas leaving the reforming unit is higher than the content in the reformer unit feed gas. If tail gas is added partially or completely downstream the

reformer unit, then the ratio of hydrogen to higher hydrocarbons in the ATR feed stream is higher than when the reformer unit is not present. Higher hydrocarbons and especially unsaturated compounds are known to react thermally (crack) into carbon species at elevated temperatures. This can be represented by the following reaction:



Since a larger amount of hydrogen is present in the process of the invention, the risk of thermal cracking is reduced and/or the tail gas may be preheated to a higher temperature.

In the case where the tail gas is added upstream the reformer unit, none or a very minute amount of higher hydrocarbons are present in the reformer outlet stream. In this case the risk of cracking from higher hydrocarbons has been eliminated.

Regardless of whether the tail gas is added before or after the reformer unit, the hydrogen content is higher and the hydrocarbon content lower than if no reformer unit was present. This has a favourable influence on the limits for soot formation in the ATR. This means that for given operating conditions the margin to soot formation is increased. Alternatively, the ATR can be operated at more severe conditions (e.g. by reducing the S/C-ratio) while maintaining an adequate margin to soot formation.

The catalytic activity for steam reforming in the reformer unit can be obtained either by conventional fixed beds of (pellet) catalysts or by catalysed hardware. In the latter

case catalytic material is added directly to a metal surface. The catalytic coating of a metal surface (wash coating) is a well known process (a description is given in e.g. Cybulski, A., and Moulijn, J. A., Structured catalysts and reactors, Marcel Dekker, Inc, New York, 1998, Chapter 3, and references herein). The appropriate material, preferably a ferritic steel containing Cr and/or Al, is heated to a temperature preferably above 800 C in order to form a layer of Cr and/or Al oxide. This layer facilitates a good adhesion of the ceramic to the steel. A thin layer of a slurry containing the ceramic precursor is applied on the surface by means of e.g. spraying, painting or dipping. After applying the coat the slurry is dried and calcined at a temperature usually in the region 350-1000 C. Finally the ceramic layer is impregnated with the catalytic active material. Alternatively the catalytic active material is applied simultaneously with the ceramic precursor. This can in the present invention either be directly to a channel wall in which the process gas flows or attached to a metallic element. In the latter case the metallic elements can be placed in the channel in which the process gas flows. The metallic element may be either in form of a monolith or cross-corrugated structures. Further catalyst hardware is in form of catalyst being deposited in metallic or ceramic structure, which is adhered to wall of the reactor. The amount of catalyst can be tailored to the required catalytic activity for the steam reforming reactions at the given operating conditions. In this manner the pressure drop is lower and the amount of catalyst is not more than needed which is especially an advantage if the costly noble metals are used. In more conventional applications with pellets, the steam reforming reactors are often designed to maximise heat transfer and pellets are simply placed in

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channels where the process gas flows often resulting in a vast excess of catalytic activity.

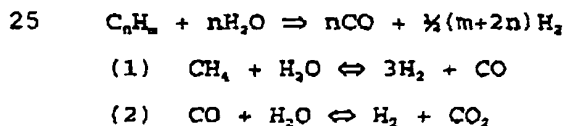
5 Similar advantages can be obtained if ceramic monoliths or cross-corrugated ceramic structures are used.

10 Reference is made to Fig. 2 in which a specific embodiment of the invention is illustrated. The tail gas (2) is pre-heated by heater or heat exchanger (3) giving a heated tail gas stream (4).

A hydrocarbon containing feedstock (1) is treated in a number of sequential steps comprising the following (two sequential steps are shown in Fig. 2):  
15 Optional addition of tail gas (5) resulting in heat exchanger feed stream (6)

20 Heating heat exchanger feed stream (6) resulting in stream (8) and optionally adding to stream (8) an amount of tail gas (9) to form reactor feed stream (10).

Passing the reactor feed stream (10) into an adiabatic steam reforming reactor (11) in which the following reactions occur:



30 These steps are continued until the desired temperature and exit gas composition is obtained. The effluent (12) from the last of the reactors can optionally be mixed with tail gas (13) to form the combined stream (16). This stream may be further heated in heater or heat exchanger (14) giving stream (17). Tail gas may optionally be added to this

stream to form the ATR feed stream (18). The ATR feed stream (18) and oxidant (19) is fed to the ATR (20) in which synthesis gas is produced and withdrawn as product stream (21).

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The hydrocarbon containing feed stream may be pre-reformed in an adiabatic pre-reformer prior to steps 1-3) above. The heat source for the heat exchangers is one or more hot gas streams not shown in Fig. 2.

10

This concept has a number of advantages in addition to those described earlier:

- Complete decoupling of the reactor design and heat exchanger (or heater design)
- Easier change of catalyst
- Higher hydrogen to olefin ratio and higher steam to higher hydrocarbon ratio at the inlet to the adiabatic reactors if the tail gas is injected at several locations. This means that the risk of forming detrimental carbon on the catalyst is reduced
- Tailoring catalysts to the different operating conditions in the adiabatic reactors. One example is to use Nickel based catalysts in the first reactor(s) where the temperature is lowest and use noble metals in subsequent reactors. Often the amount of steam needed to avoid carbon formation increases with temperature. Since noble metals are more resistant to carbon formation than Nickel, these should be used at the higher temperatures.

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25  
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The heat source for the reformer unit may be either from a fired heater or a hot process gas from elsewhere in the plant including the effluent from the ATR. The former alternative may have the disadvantage that additional natural gas or another hydrocarbon feedstock may have to be burned

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to provide the necessary heat. Part of this heat may be recovered by preheating the tail gas and/or the feed for the adiabatic pre-reformer by using the effluent from the ATR.

## 5 EXAMPLES

### Example 1

Natural gas with a composition of 95% methane, 3.5% ethane, and 1.5% propane is used. It is assumed that the tail gas  
10 in all examples has the composition given in Table 1.

Table 1

Tail gas composition used in examples

Compound	Concentration (mole %)
Hydrogen	31.1
Carbon Monoxide	27.8
Methane	3.7
Nitrogen	4.0
Carbon Dioxide	30.4
Ethane	1.5
Ethylene	1.5

15

### Example 1A

Example 1A is a comparative example. In this case the desulphurised natural gas is mixed with steam and the resultant mixture is heated to 430°C and fed to an adiabatic  
20 pre-reformer. The pre-reformed mixture is heated to 600°C and mixed with tail gas which is preheated to 200°C. The resultant mixture is fed to the ATR together with an oxidant (oxidant composition: 99.5% oxygen and 0.5% Argon) in  
25 which the synthesis gas is produced. The amount of tail gas



added is adjusted to give a hydrogen-to-carbon monoxide ratio in the synthesis gas stream equal to 2.00. The ATR effluent temperature is 1050°C. All reactions are assumed to be in equilibrium at reactor outlet conditions. The pressure throughout the system has artificially been set to 2.48 MPa and pressure drops have been neglected.

In all cases the steam-to-carbon ratio is 0.6.

10 **Example 1B**

Example 1B is also a comparative example. The only difference is that the tail gas is mixed into the natural gas and steam mixture upstream the adiabatic pre-reformer. The inlet temperature to the adiabatic pre-reformer is 430°C.

15

**Example 1C**

This is similar to example 1A except that the pre-reformer effluent is further steam reformed in a reformer unit in accordance with the present invention. The gas leaving the reforming unit is assumed to be in equilibrium at 600°C before the tail gas is added.

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**Example 1D**

This example is identical to example 1C except that the tail gas is added to the effluent from the adiabatic pre-reformer.

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In Table 2 the production of synthesis gas is given relative to the natural gas and oxygen consumption. Also given is the hydrogen-to-ethylene ratio in the ATR feed stream.

30

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Table 2

Production of synthesis gas relative to the natural gas and oxygen consumption.

Example	Synthesis gas production (Nm3 syngas produced/Nm3 oxygen consumed)	Synthesis gas production (Nm3 syngas produced/Nm3 oxygen consumed)	Hydrogen-to-ethylene ratio in ATR feed stream
1A	5.09	3.16	40
1B	5.00	3.14	Inf.
1C	5.47	3.23	101
1D	5.29	3.19	Inf.

5 Inf=infinite

10 It is seen from Table 2 that the amount of synthesis gas produced increases regardless of whether the tail gas is added upstream or downstream the reformer unit. The addition of tail gas to the adiabatic pre-reformer decreases the productivity. The hydrogen to ethylene ratio is higher in example 1C than in example 1A, which is a further advantage of the inventive process, when tail gas is added upstream the ATR.

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**CLAIMS**

1. Process for the production of synthesis gas from a hydrocarbon feed stock comprising the steps of endothermic  
5 and/or adiabatic catalytic steam reforming and autothermal steam reforming in series, wherein the steam reforming is carried out in one or more endothermic stages in series and/or in one or more adiabatic steam reforming stages in series with intermediate heating of feed stock gas leaving  
10 the adiabatic reforming stages and wherein carbon monoxide rich gas is added prior to at least one of the endothermic or adiabatic steam reforming stages and/or prior to the autothermal steam reforming step.
- 15 2. Process of claim 1, comprising the further step of adiabatic pre-reforming the feed stock prior to the endothermic or adiabatic steam reforming.
- 20 3. Process of claim 1, wherein the endothermic or adiabatic steam reforming is performed in presence of catalysed hardware.
- 25 4. Process of claim 3, wherein the catalysed hardware is in form of a ceramic monolith or a cross-corrugated ceramic structure.
5. Process of claim 1, wherein the endothermic steam reforming step is performed in heat conducting relationship with a hot process gas.
- 30 6. Process of claim 5, wherein the hot process gas is an effluent stream from the autothermal reforming.

7. Process of claim 1, wherein the intermediate heating of the reacting feed stock is performed in heat conducting relation ship with a hot process gas.

5

8. Process of claim 7, wherein the hot process gas is an effluent stream from the autothermal reforming.

9. Process according to any one of the preceding claims, wherein the carbon monoxide rich gas comprises tail gas from a Fischer -Tropsch process.

10. Steam reforming system for use in a process for the production of synthesis gas from a hydrocarbon feed stock comprising  
15 optionally a pre-reformer for adiabatic pre-reforming of the feed stock;  
a reformer for endothermic catalytic steam reforming and/or at least a first and last adiabatic catalytic steam re-  
20 former connected in series;  
means for intermediate heating of the feed stock between the at least first and last adiabatic steam reformer;  
a down stream autothermal steam reformer connected in series with the reformer for endothermic steam reforming or  
25 with the last adiabatic steam reformer; and  
means for addition of a carbon monoxide rich gas upstream the endothermic steam reformer or upstream of the at least first and/or last adiabatic reformer and/or upstream of the autothermal reformer.

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**ABSTRACT**

5 Process and system for the production of synthesis gas from  
a hydrocarbon feed stock comprising the steps of endother-  
mic and/or adiabatic catalytic steam reforming and auto-  
thermal steam reforming in series, wherein the steam re-  
forming is carried out in one or more endothermic stages in  
series or in one or more adiabatic steam reforming stages  
10 in series with intermediate heating of feed stock gas leav-  
ing the adiabatic reforming stages and wherein carbon mon-  
oxide rich gas is added prior to at least one of the endo-  
thermic or adiabatic steam reforming stages and/or prior to  
the autothermal steam reforming step.

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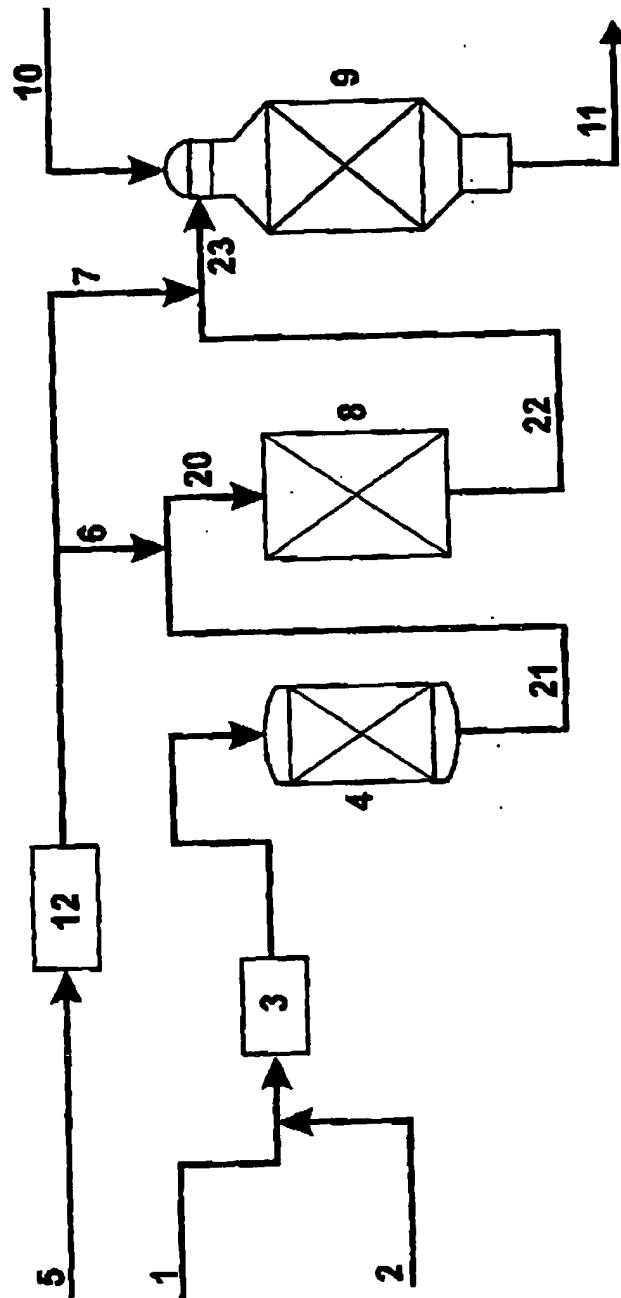


Fig. 1

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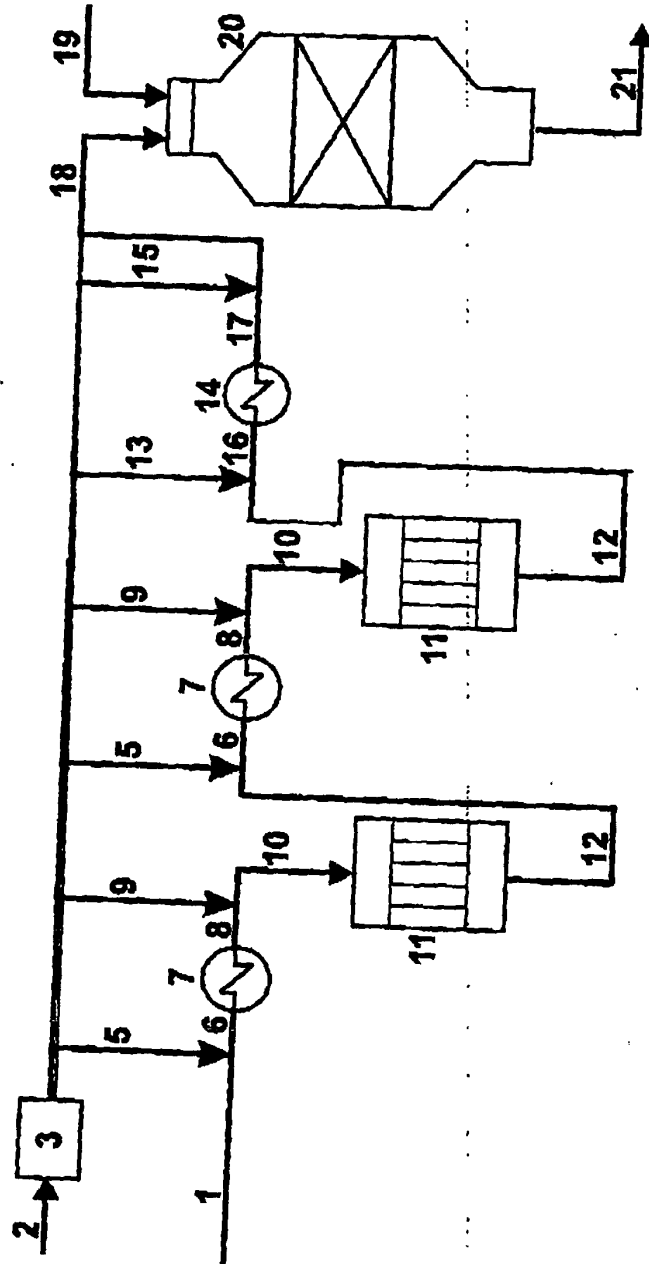


Fig. 2

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